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Regional Transport and Transformation of Sulfur Dioxide to Sulfates in the United States

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Reduction of sulfate concentration levels will require strenuous efforts to control SO_2. Also, large new additions to utility capacity in western areas may lead to significant increases in western sulfate concentration levels. The types of research activities required to quantitate crucial experimental parameters are discussed.

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REGIONAL TRANSPORT AND TRANSFORMATION OF SULFUR DIOXIDE TO SULFATES IN THE UNITED STATES

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ABSTRACT

The trends in and relationships between ambient air sulfur dioxide and sulfate concentrations at 48 urban and 27 nonurban sites throughout the United States between 1963 and 1974 have been analyzed. Large decreases in sulfur dioxide concentrations at urban sites in the eastern and midwestern United States have been accompanied by modest decreases in sulfate concentrations. Large variations in sulfur dioxide emissions among air quality control regions also result in much smaller variations in sulfate concentrations. Large changes in the patterns of sulfur oxide emissions have little impact on sulfate concentrations in most air quality regions. Comparisons of air quality regions with similar sulfur dioxide emission levels and patterns of emissions in the eastern and western United States and of sulfur dioxide, sulfate, and vanadium relationships between urban-suburban and urban nonurban sites lead to the same conclusion. Long-distance sulfur oxide transport with chemical conversion of sulfur dioxide to sulfates over ranges of hundreds of kilometers or more provides a consistent explanation for all of the observed results. This conclusion has been suggested earlier, and the present analysis strongly supports previous discussions.

Reduction of sulfate concentration levels will require strenuous efforts to control sulfur oxides not only locally but throughout large geographical regions. Also, large new additions to utility capacity in western areas may lead to significant increases in western sulfate concentration levels. The types of research activities required to quantitate crucial experimental parameters are discussed.

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SECTION 1

INTRODUCTION

BACKGROUND

Previous discussions have been published on the distribution of concentrations of sulfur dioxide and sulfate in the United States.[1,2] A relationship between annual sulfur dioxide and sulfate concentrations was suggested.[1] It was pointed out that elevated sulfate concentrations appear to be widely distributed throughout entire regions in the eastern and midwestern United States.[1,2] These uniformly high sulfate levels were attributed to long-range transport, with transformation of sulfur dioxide to sulfate well downwind of urban areas.[1,2] An anthropogenic background was suggested as present throughout the eastern United States and a portion of the midwestern United States.[1,2]

This position has received acceptance in the recent National Academy of Sciences report on the sulfur oxide and nitrogen oxide pollution from combustion sources.[3] However, some aspects of the contribution of transport and transformation to urban and nonurban concentrations are still being debated.[3,4] The need for continuing analysis of the available measurements of sulfate and sulfur dioxide is clear. Decisions on fuel usage patterns and placement of fossil-fuel power plants may be influenced by improved understanding of the processes of sulfate formation, transport, and removal.

Additional sulfate and sulfur dioxide measurements now are available beyond data bases used earlier.[1,2] Sulfate measurements are available at many sites into the 1970's. Detailed sulfur dioxide emission inventories and fuel usage patterns are available for recent years.[5,6] It is essential to utilize this additional data base in determining evidence bearing on the regional distribution patterns for sulfates.

PROCEDURES

Sulfur dioxide and sulfate concentrations were obtained by the National Air surveillance Networks from the early 1960's into the 1970's using a 24-hour average sampling period once every 2 weeks during each year. Results were utilized for sites having as a minimum several years of concurrent measurements for sulfur dioxide and sulfate (probably including sulfite and sulfide, if present). In addition to the previous cited sources,[1,2,7,8] several new publications[9-12] have been utilized. Methods of analysis have been reported previously.[1] Three-year running averages were computed as the best available means of smoothing out the effects on sulfur dioxide emissions and air quality of varying severities of winter or summer seasons.

In addition to sites located well within urban areas, a number of sites in nonurban locations exist. Measurements at such sites usually start in 1965, but began earlier at a few locations. These nonurban sites vary from suburban-rural locations in the eastern United States to rather remote sites at some western locations. These sites were not originally selected to necessarily represent the most remote sites geographically available. Logistical requirements as to available sites, power, volunteer services for replacement of filters, and related operational needs had to be considered in the site selections. In the eastern United States, it is difficult to find sites that are well removed from all power plants, petroleum activities, paper mills, or some form of industrial activity. Also, the primary intent was not to find sites for measurements of geophysical significance, but to represent the concentrations of pollutants people in suburbs, towns, villages, or rural environments would be exposed to by all surrounding anthropogenic activities. Some local influences do exist; however, this is the only body of measurements ever carried out in the United States that is available to evaluate the potential for regional transport and transformation of sulfur oxides to sulfates in the United States.

Concern has been expressed about conversion of some of the sulfur dioxide present to sulfate on the glass fiber filters used because of the alkaline nature of the filters. However, this problem usually is oversimplified. Simulated laboratory measurements are of limited use in estimating whether or not significant conversion has occurred. To reconstruct the circumstances historically at each of many sites with respect to both filter and matrix is a very difficult, if not impossible, task.

A few comments can be made based on the observed measurement results for sulfur dioxide and sulfate. If conversion of sulfur dioxide to sulfate on the filter substrate were a significant factor, the conversion was not at all in proportion to sulfur dioxide concentration. This type of artifact might be expected to result in large decreases in sulfate concentrations with large decreases in sulfur dioxide concentrations. Such decreases have not been observed. In fact, high sulfate concentrations occurred in nonurban sites where sulfur dioxide concentrations were very low and also where possible catalytic metal species also are at very low concentrations.

A recent investigation of sampling and analysis of sulfates involved collection in Los Angeles, Calif., St. Louis, Mo., and Durham, N. C., of both high volume samples on glass fiber filters and of low volume samples on fluoropore filters.[13] There is no indication of sulfur dioxide to sulfate conversion on fluoropore filters. The analytical results using the methyl thymol blue method on the two types of filter samples from the three sites gave ratios of concentration ranging between 0.97 and 1.04 to 1. Such results indicate that an insignificant percentage of the sulfate measured originated from sampling artifacts on 24-hour high volume samples on glass fiber filters.

CHARACTERISTICS OF SULFATE PARTICLES

The amount of sulfate available to undergo transport depends on the characteristics of sulfate particles, the rates of transformation of sulfur dioxide to sulfate, and the removal processes for sulfur dioxide and sulfate.

Particle size distribution measurements for sulfates or particulate sulfur are available at sites in Philadelphia, Pa., Cincinnati, Ohio, Chicago, Ill., St. Louis, Mo., Los Angeles, Calif., and San Francisco, Calif.[14-18] The mass median diameters were computed to range from 0.2 to 1 um, with most of the MMD values between 0.2 and 0.6 um. From 80 to over 90 percent of the sulfate or particulate sulfur was found to occur in the size range below 2 um. Analysis for ammonium ion at the same sites in Philadelphia, Cincinnati, and Chicago indicated that the ammonium ion has almost the same particle size range characteristics as sulfate.[19] Measurements at sites in Los Angeles, Calif., New York, N. Y., and Columbus, Ohio, and Dayton, Ohio, tend to indicate that either $(NH_4)_2SO_4$ or NH_4HSO_4 may be the predominant species.[20-23]

Whatever the chemical form of sulfur-containing particles, their particle size characteristics will result in a very slow rate of removal by dry deposition or uptake by foliage. Sulfur dioxide would be much more rapidly removed by foliage and other surfaces. Except during periods of precipitation, the conditions of emission and surface removal of sulfur dioxide should be critical. Conversion rates of sulfur dioxide to sulfate in urban and power plant plumes are reported in the 1 to 20 percent per hour range.[24] The rate of dry deposition appears to be in the same range [25-27] However, the rates for these two major competing processes may vary considerably, with one or the other process dominating in the same or different areas depending on a number of emission and atmospheric parameters.

It is not the purpose of this analysis to discuss the characteristics of the finely divided particulate fraction of the total suspended particulates in the atmosphere. However, some facts with respect to sulfates are appropriate to consider briefly. First, sulfates constitute the following average percentage of total suspended particulates at urban sites in various regions of the United States: east coast, 15 percent; midwest (east of Mississippi), 10 percent; southeast, 8 percent; midwest (west of Mississippi), 6 percent; mountain states, 4 percent; southwest, 5 percent; west coast, 9 percent. These results suggest that sulfates constitute a significantly more important fraction of the total suspended fraction in

the eastern United States than in the western United States. At nonurban sites, sulfates show the same relative regional patterns, except that sulfates constitute a larger portion of total suspended particulates at nonurban compared to urban sites for most regions of the United States. The average percentage of sulfate in the finely divided particulate (sum of sulfate, benzene-soluble organics, nitrates, and lead) by region at urban sites in 1968 thru 1970 were as follows: east coast, 61 percent; midwest (east of Mississippi) 59 percent; southeast, 50 percent; midwest (west of Mississippi), 47 percent; mountain states, 36 percent; southwest, 40 percent; west coast, 39 percent. At nonurban sites, the same relative regional patterns were observed, except that sulfates constituted a significantly larger portion of the finely divided species at nonurban compared to urban sites in all regions of the United States.

SECTION 8

RELATIONSHIPS FOR SULFUR DIOXIDE AND SULFATES AT URBAN SITES

Sufficient annual average sulfur dioxide and sulfate concentration data existed at 48 urban sites to permit computation of 3-year running averages for the period 1963 through 1974. However, even at these sites, the monitoring results were incomplete during portions of the periods, particularly for sulfur dioxide concentrations. Vanadium measurements are available, and they can be associated with the sulfur-containing emission products from oil-fired combustion units, so these results are also included for east coast sites. The available results are listed in Tables 1 to 6. These sites are grouped on a regional basis as follows: east coast (north of Virginia), midwest (east of Mississippi), southeast, midwest (west of Mississippi), interior western states including the mountain states and southwestern states, and sites on the west coast.

TRENDS IN SULFATE CONCENTRATIONS

The overall averages by region for sulfur dioxide and sulfate show consistent trends (Tables 1-6). Throughout the 1963 to 1974 period, or the portion thereof for which sufficient measurements were available, the order of decreasing sulfur dioxide and sulfate concentrations were as follows: (1) east coast, and midwest (east of Mississippi), (2) southeast, (3) west coast, (4) midwest (west of Mississippi), (5) western states. Sites in western states or in midwestern states west of the Mississippi have had sulfur dioxide concentrations averaging 10 to 20 percent of the concentrations at sites on the east coast. The range of sulfate concentrations is smaller. Sulfates averaged over western sites have ranged from 30 to 70 percent of the sulfate concentrations at east coast and midwestern (E) sites.

Sulfur dioxide concentrations definitely trended downward between the mid-1960's and early 1970's at east coast and at many midwest urban sites east of the Mississippi (Tables 1,2). These downward trends in ambient air sulfur dioxide concentrations are consistent with the decreases in sulfur dioxide emissions in these areas. A smaller downward trend in sulfur dioxide may have occurred at southeastern urban sites and urban sites west of the Mississippi, but the sulfur dioxide results at these sites are too incomplete or the concentrations too low to be certain as to the trends (Tables 3-6). Sulfate concentrations did not show proportional downward trends with sulfur dioxide concentrations in any of the regions. While the average sulfur dioxide concentrations decreased by 58 percent at east coast urban sites between 1963-65 and 1969-71, the sulfate concentrations decreased by 15 percent (Table 1). At midwestern urban sites (east of Mississippi), the average sulfur dioxide concentrations decreased by 30 percent between 1965-67 and 1969-71; the sulfate concentrations fluctuated somewhat but show no significant trends on the average at urban sites. As a result by the 1970's the average regional concentrations of sulfate in the midwest (E), exceeded those on the east coast (Table 1,2) at urban sites.

Along the east coast from Providence, R. I. to Baltimore, Md., there was a slow decrease in sulfate concentrations. Comparing the 1972-74 period with 1964-66 sulfate concentrations decreased by from 18 to 42 percent. The largest decreases were around New York city, N. Y. and Philadelphia, Pa. Therefore, there was a consistent increase in sulfate concentrations in most east coast urban sites.

In most of the other regions no trend in sulfate concentrations was evident or the data was too limited to discern such trends. The exception was for sulfates in the southwest and mountain states where an upward trend in sulfate occurred at a number of the urban sites.

It appeared possible that, while annual average sulfate concentrations did not decrease in proportion to changes in annual average sulfur dioxide concentrations, a different relationship would be obtained using higher percentile sulfate concentrations. Various such comparisons were computed.

the most favorable relationship was obtained using 80th percentile sulfate concentrations, but the improvement was modest. For example, sites in six cities -- New York, N. Y., Newark, N. J., Baltimore, Md., Pittsburgh, Pa., Indianapolis, Ind., and St. Louis, Mo. -- over the 1963-65 to 1970-72 period showed an averaged decrease in annual average sulfur dioxide concentrations of 63 percent and a range from 39 percent to 74 percent decrease in sulfur dioxide. For the same sites and time period, the annual average sulfates and 80th percentile sulfates showed an average decrease of 10 and 18 percent, respectively, and a range from 20 percent increase to 37 percent decrease and from a 3 percent increase to a 45 percent decrease, respectively. Therefore, the choice of statistical measures of sulfate concentration other than arithmetic annual averages also does not result in anything like a proportional relationship between sulfur dioxide and sulfates.

SULFUR DIOXIDE EMISSIONS AND SULFATE CONCENTRATIONS

The influence of variations in sulfur dioxide emissions on sulfate concentrations can be examined by use of available results in several air quality control regions. In the midwest, some air quality control regions, including Pittsburgh, Pa., Detroit, Mich., Cleveland, Ohio, Chicago, Ill., and St. Louis, Mo., had annual sulfur dioxide emissions (1972) from 700,000 to 1,200,000 tons/year. The annual average sulfate concentrations (1970-72 or 1969-71) in these regions (Table 2) ranged from 14 to 20 ug/m^3 and averaged 16.7 ug/m^3. Other air quality control regions in the midwest, including Columbus, Ohio, Dayton, Ohio, and Indianapolis, Ind., had annual sulfur dioxide emissions of 100,000 to 200,000 tons/year. At these sites annual average sulfate concentrations (1970-72) ranged from 12 to 14 ug/m^3 and averaged 13.0 ug/m^3. Therefore, the air quality control regions with sulfur dioxide emissions five to ten times higher than regions with the lower sulfur dioxide emissions had sulfate concentration levels only 28 percent higher. These results demonstrate the low sensitivity of sulfate concentrations to large differences in sulfur dioxide emissions originating within the same air quality control region at least in the midwestern United States.

EFFECT OF ISOLATED COMPARED TO NONISOLATED REGIONAL CONDITIONS ON SULFATES

Another comparison that can be made is between urban sites within air quality control regions that are relatively isolated and those that are not isolated. The term isolated is used in the context of a region surrounded by other regions with relatively low sulfur dioxide emissions from utility or other emissions sources. The areas including Minneapolis-St. Paul, Minn., and Kansas City, Mo., are examples of relatively isolated air quality regions. The sulfur dioxide emissions within these regions is in the range of 200,000 tons/year (1972).[5] Utility sources contribute 72 and 81 percent of the sulfur dioxide emissions, while area sources contribute 9 and 8 percent respectively, in these two regions.[5] A number of air quality regions east of the Mississippi also have sulfur dioxide emissions in the 200,000-ton/year range.[5] These regions are surrounded within 100 miles or less by other air quality regions emitting sulfur dioxide in amounts equal to or much larger than 200,000 tons/year. Such air quality regions include Providence, R.I., Hartford-New Haven-Springfield, Conn., Baltimore, Md., Washington, D. C., and Indianapolis, Ind. In this latter group of air quality control regions, utility sources contributed an average of 62 percent (range 51 percent to 76 percent) of the sulfur dioxide emissions, while area sources contributed an average of 21 percent (range 9 to 35 percent of sulfur dioxide emissions.)[5] In the two isolated regions, annual average sulfate concentrations (Table 4) were 7 to 8 ug/m^3 (1970-72), while for the nonisolated regions annual average sulfate concentrations (Tables 1, 2) were 12 to 16 ug/m^3, about twice the sulfate concentrations in the isolated regions.

It might be suggested that differences in sulfur dioxide emission patterns within air quality regions might have a significant effect on ambient air sulfate concentrations. For example, the lower quantities of near-surface area emissions of sulfur dioxide in the two isolated regions, rather than the isolation of the regions, might be responsible for the lower ambient air sulfate concentrations. However, this hypothesis is not supported by comparisons of the annual average sulfate concentrations

within the five nonisolated regions discussed above. Despite a range of 9 to 35 percent in the near-surface area emissions within these regions, there are no significant differences in the averaged annual sulfate concentrations. The Indianapolis and Baltimore air quality regions are the two nonisolated regions with comparable area sulfur dioxide emissions to the Minneapolis-St. Paul and Kansas City air quality regions. The averaged annual sulfate concentrations in the two nonisolated regions averaged 14 ug/m^3, about twice the sulfate concentrations in the isolated regions. Therefore, comparisons of sulfate concentrations at sites in isolated and nonisolated regions with comparable area sulfur dioxide emissions support isolation as the dominant factor in accounting for differences in regional sulfate concentration levels.

It also might be suggested that some other factors of a meteorological nature, such as differences in temperature, solar radiation, mixing heights, wind speed, or precipitation, might be significant in explaining differences in these sites in sulfate concentrations. Differences in solar radiation and wind speeds are small among sites in most of the eastern and midwestern United States and are somewhat higher for the east coast sites than midwest sites, but the mean annual afternoon mixing heights are nearly the same for all of these sites. The two isolated air quality regions being used for comparison have similar wind speed and mixing height characteristics compared to other midwestern sites. However, the temperatures throughout the year in Minneapolis are lower and the annual precipitation in the form of rain is lower than at sites further east. Kansas City does have a climatological pattern nearly the same as a number of nonisolated midwestern sites. The sulfate concentrations at the site in Kansas City were consistently less than 1 ug/m^3 greater than at the site in Minneapolis. Therefore, if these climatological factors have an influence on sulfates, the effect is very small.

With isolation as the dominant factor, it follows that at least half of the sulfate concentrations measured at eastern urban sites can be attributed to sulfur oxide emissions being transformed to sulfate during transport from adjacent regions. This contribution can be an interregional contribution

of sulfates. This contribution actually may exceed 50 percent because some small interregional contribution to sulfates also may occur into the Minneapolis-St. Paul and Kansas City regions.

EFFECTS OF SHIFTS IN SULFUR DIOXIDE EMISSION PATTERNS ON SULFATE CONCENTRATIONS

Although there already has been some discussion of shifts of sulfur dioxide emission patterns on sulfate concentrations, additional comparisons among regions should be considered. One comparison that can be made involved selecting air quality control regions with the same annual sulfur oxide emissions, but significantly different contributions to the total emissions from area sources. The regions compared also should either be all nonisolated or all isolated from large extraregional sources. Among the appropriate regions for comparison were four nonisolated regions -- Providence, R.I., and Hartford-New Haven-Springfield, Conn., with higher area sources and Baltimore, Md., and Indianapolis, Ind., with lower area emissions.[5] The total sulfur oxide emissions, utility emissions, and area emissions in 1972 for Providence and Hartford-New Haven-Springfield averaged 216,000 tons/year, 123,000 tons/year, and 67,000 tons/year, respectively. The total sulfur oxide emissions, utility emissions, and area emissions in 1972 for Baltimore and Indianapolis averaged 218,000 tons/year, 131,000 tons/year, and 24,000 tons/year, respectively.[5] Therefore, the former two regions had almost three times the loadings of area sulfur oxide emissions compared to the latter two regions. The 1970-72 averaged sulfate surface concentrations were 13.6 ug/m^3 for Providence and Hartford-New Haven-Springfield and 14.2 ug/m^3 for Baltimore and Indianapolis (Table 2). Examination of other pairs of regions with about the same sulfur oxide emission but different proportions of area-wide emissions also did not show higher sulfates in regions with higher near-surface-level area sulfur oxide emission sources.[5] Therefore, the available results do not appear to demonstrate that near-surface area sulfur oxide emissions contribute any more per ton of emissions than point source emissions to urban surface sulfate concentrations. This conclusion applies to the northeastern and midwestern United States.

Most western urban sites have sulfate concentrations two to three times lower than midwestern sites east of the Mississippi and in the northeastern United States. Many of the western regions in which these sites are located

have had negligible sulfur oxide emissions from utility sources because of the use of gas or hydroelectric power to generate electricity. Often industrial emissions from the primary metal industries or from the petroleum and petrochemical industries are the predominate sources of sulfur oxides. Therefore, in addition to such regions usually being largely isolated from extraregional sulfur oxide emissions, they also have drastic differences in sulfur oxide emission patterns compared to eastern sites. Regions such as the ones including Houston, Texas, and Seattle, Wash., are examples of such types of regions. Since these western regions have nearly the same sulfate concentrations as regions such as Minneapolis-St. Paul and Kansas City, which have emission patterns more typical of eastern regions, isolation of these regions from extraregional sulfur oxide emissions again appears to be substantially more important than the shifts in the sulfur oxide emission patterns within the region.

A possible exception to the above discussion of the influence of sulfur oxide emission patterns on sulfate concentrations may occur in the Southern California air quality region. Sulfate concentrations in this region are significantly higher than in other western regions. Although utility sources are more significant in the Southern California air quality region than in most other western regions, the utility contribution was only 17 percent in 1972. Area sources contributed 46 percent, with transportation sources alone contributing 11 percent to sulfur oxide emissions. This region had about the highest proportion of area-wide sulfur dioxide emissions in the United States and an atypically high transportation component. The sulfate concentrations measured in this region are in the lower end of the range of sulfate concentrations in the eastern United States. The southern California air quality region is relatively well isolated from sulfur oxide emissions from other regions.

Several factors could contribute to the higher sulfate concentrations -- for a western area -- in the Southern California air quality region (Table 6). These factors include high photochemical activity for conversion of sulfur dioxide to sulfate, poorer ventilation, and the higher near-surface area emissions.

There is a gradient in sulfur oxide emissions from near the Pacific coast, through the western portion of the Los Angeles basin, to the eastern portion of the basin. All sources of sulfur oxide emissions are denser in the western portion of the region -- utility, industrial, and transportation sources. Much lower sulfur dioxide concentrations at sites in the eastern portion of the region support the existence of such a gradient. Nevertheless, the sulfate concentration levels are almost the same in the western and eastern portions of the region (Table 6). This observation is consistent with a flux of sulfur dioxide being transported, with rapid transformation to sulfate from the western to eastern portions of the region. These facts indicate that photochemistry and local meteorology are likely to be the important factors in explaining the higher sulfate concentrations. The high surface sulfur oxide emissions in this region are probably an interacting factor because these surface emissions of sulfur oxides can mix rapidly with the hydrocarbon and nitrogen oxide precursors to photochemical reactions that cause conversion of sulfur dioxide to sulfates. It also is reasonable that the relatively arid conditions in this region result in lower rates of removal by deposition to vegetation of near-surface area sulfur dioxide emissions compared to eastern regions. This circumstance results in a larger fraction of sulfur dioxide being available for conversion to sulfate. Therefore, the Southern California air quality region may be a very special case with respect to the significance of area compared to point emission contributions to sulfur oxide emissions.

SECTION 9

RELATIONSHIPS FOR SULFUR DIOXIDE AND SULFATE AT NONURBAN SITES

Sufficient annual average sulfate concentration data existed at 27 nonurban sites to permit computation of 3-year running averages for the period 1965 through 1973. There were incomplete results at a number of sites. Sulfur dioxide concentrations were occasionally available for several years in the late 1960's and early 1970's at some sites. Vanadium concentrations were available during periods of several years at the non-urban sites on the east coast. These results are tabulated in Table 7.

By region, the order of decreasing sulfate concentrations were as follows: (1) east coast and midwest (east of Mississippi), (2) southeast, (3) southwest, (4) midwest (west of Mississippi) and west coast, (5) mountain states. Sulfate concentrations in mountain state sites are only 15 to 25 percent of the sulfate concentrations at east coast or midwestern (east of Mississippi) sites.

Upward trends or no trends in sulfates occurred at most nonurban sites on or near the east coast (Table 7). This is in contrast to the downward trends at most urban sites in this same geographical area.

There also was an upperward trend in sulfate concentrations at the nonurban sites in the midwest (E) from the 1960's into the 1970's. This trend would be consistent with overall increases in sulfur oxide emissions from utility sources in this region during this period. Upward trends in sulfate concentrations were apparent for many western nonurban sites.

Sulfur dioxide concentrations were low at all nonurban sites. No clear trends could be observed at these low concentration levels.

Three-year running averages for nonurban sulfate on the east coast and in the midwest east of the Mississippi River equal or exceed the corresponding averaged sulfate concentrations at urban sites in regions west of the Mississippi (Tables 4-6). The sulfates in the Los Angeles basin area do exceed levels at eastern and midwestern nonurban sites, but sulfate concentrations at other west coast urban sites do not exceed the nonurban sulfate concentrations at eastern sites.

The possibility for a natural or background biogenic contribution to sulfate concentrations should be considered. At most sites, there is little or no evidence for such a contribution being significant. One possible exception is the very isolated nonurban site on Cape Hatteras. This site might be expected to be influenced only slightly by transport of sulfur oxides from urban areas, since it is more isolated from urban contributions than other eastern nonurban sites. Nevertheless, the sulfate concentrations are substantially elevated at Cape Hatteras. The surrounding area to the west of Cape Hatteras for 100 miles and more consists of shallow coastal waters, with much swamp and marsh land and only a small number of small towns and light industrialization. Therefore, it can be hypothesized that natural sulfur gases are being oxidized in this area in appreciable amounts to sulfate. However, measurable vanadium concentrations at this site indicate the possibility for transport even to the site from the coastal areas of Virginia where appreciable quantities of high vanadium content oil are utilized.

If a tropospheric or continental concentration background exists for species formed directly or indirectly from natural sources or for long-lived species emitted from anthropogenic sources, a minimum concentration will be detectable. If such a minimum exists, it should be evident in an examination of the distribution of minimum 24-hour sulfate concentrations at nonurban sites over a period of years.

An examination of the data base at nonurban sites was made for the years 1966 to 1972. Minimum 24-hour sulfate concentrations at or below 1 ug/m^3 occurred for eastern nonurban sites. At western nonurban sites, minimum 24-

hour sulfate concentrations at or below 1 ug/m^3 were frequent. Since the detection limit for sulfate in the analyses was 0.6 ug/m^3, concentration values at or below this level have no numerical significance, although a substantial number of such very low sulfate values do appear as minimum concentrations at western sites. If a natural background of sulfates does exist, this data base indicates that it probably occurs at less than 3 ug/m^3. Such a background is far too small to influence the distribution patterns of sulfate over the United States. Special situations where sites are downwind of strong natural sources should be evaluated on an individual basis.

SECTION 4

RELATIONSHIPS BETWEEN URBAN AND NONURBAN SITES

RELATIONSHIPS BETWEEN URBAN AND SUBURBAN SITES ON THE EAST COAST

A comparison of measurements in the core area of a metropolitan area with those in surrounding suburban towns and villages can be made. Measurements are available for sulfur dioxide, sulfates, and vanadium at two sites within Philadelphia and Camden and at seven sites in surrounding towns and villages in Pennsylvania and New Jersey. The measurements were made over the 1964 to 1971 period at the sites in Philadelphia, Camden, and Glassboro, N.J., from 1965 or 1966 to either 1970 or 1971 at sites in Warminster, Pa., West Chester, Pa., and Burlington County, N. J. (fragmentary results are available also for sites in Marlton, Pemberton, and Bridgeton, N. J.). The results at the two urban and four suburban sites have been used to compute 3-year running averages for sulfur dioxide, sulfates, and vanadium at each site (Table 8).

The ratio of urban to suburban sulfur dioxide concentrations indicates about a four to one greater dilution of sulfur dioxide at the suburban sites. The ratio of urban to suburban sulfate concentration indicates almost a two to one greater dilution of sulfates at the suburban sites. There is a slight trend towards a greater spread between these two urban to suburban ratios with time. The ratio of urban to suburban vanadium concentrations increased from 2.8:1 to 5.7:1, with the increase in urban vanadium concentrations reflecting increased urban use of high-vanadium-content residual oil of lower sulfur content. The site in Glassboro is the only suburban site showing a consistent increase in vanadium concentration along with the urban sites in Philadelphia and Camden.

The high sulfate concentrations in the suburban sites are of particular interest and concern. By the late 1960's, the average sulfur dioxide to sulfate ratio at these suburban sites was 2:1. The sulfate concentrations at these suburban sites in the late 1960's exceeded half of the sulfate

concentrations within Philadelphia and Camden in 1965-67 when the sulfur dioxide to sulfate ratios were as high as 6:1 or 7:1. Even more striking were the sulfur dioxide to sulfate ratios of 1:1 in Glassboro in 1968-70 and 1969-71, with the sulfate concentration in Glassboro in the 1969-71 period still over half of the average sulfate concentrations in Philadelphia-Camden, while the sulfur dioxide concentration of 7 ug/m^3 was only 5 percent of the 1965-67 sulfur dioxide concentration in Philadelphia-Camden.

It is very difficult to explain such high sulfate levels in a number of suburban sites as associated dominately with local sources of sulfur dioxide emissions. The more reasonable explanation for the high sulfate concentrations at such widely scattered suburban sites around Philadelphia-Camden would be regional scale transport of sulfur dioxide with transformation of sulfur dioxide to sulfate. The combination of dilution, conversion of part of the sulfur dioxide to sulfate, and dry deposition of the remainder could account for the low sulfur dioxide to sulfate ratios observed along with the low sulfur dioxide concentrations. This discussion is not meant to suggest that there cannot be some local contributions to the sulfur content at any particular site.

RELATIONSHIPS BETWEEN URBAN AND NONURBAN SITES ON THE EAST COAST

Measurements for sulfur dioxide, sulfate, and vanadium are available for comparison of averaged concentrations at 11 urban and 6 nonurban sites east of the Appalachian and north of Virginia. In this region, high vanadium residual oil is an important utility and industrial fuel in New England, eastern New York, New Jersey, eastern Pennsylvania, Delaware, and Maryland. While the relative use of oil compared to coal decreases from New England, New York-New Jersey, down to Washington, D. C., it appears that vanadium can be used as a tracer for averaged utility and industrial combustion emissions through this region. The ratios of urban to nonurban concentrations computed from Table 1 and Table 7 are as follows:

Year	SO_2	SO_4^{-2}	V
1965-67	--	2.2:1	12:1
1966-68	--	2.1:1	7:1
1967-69	--	2.0:1	14:1
1968-70	5:1	2.3:1	12:1
1969-71	5:1	2.2:1	10:1
1970-72	--	1.9:1	--
1971-73	--	1.8:1	--
1972-74	--	1.8:1	--

The average sulfur dioxide to sulfate ratios at the urban sites ranged downward from 6:1 in the early 1960's to just over 4:1 by 1970. At the nonurban sites the sulfur dioxide to sulfate ratio was just over 1:1.

The urban to nonurban sulfate ratio is just a little higher than the previously discussed urban to suburban sulfate ratios. The urban to nonurban sulfur dioxide and vanadium ratios are two to four times greater than the corresponding urban to suburban ratios.

The high sulfate concentrations and low sulfur dioxide to sulfate ratios at the nonurban sites are especially in need of explanation. Several possible contributions to the overall concentrations at the nonurban sites need to be considered: (1) local emissions around the sites, (2) transport of species formed in eastern urban areas without further reaction to these nonurban sites, (3) transport of species formed in eastern urban areas with additional reaction during transport to these nonurban sites.

Local emissions of sulfates imply either natural emissions or manmade emissions produced locally. Natural emissions have already been discussed. It was concluded that the sulfate background under most conditions at most sites was 1 ug/m^3 or less. Since the annual average concentrations at these sites ordinarily ranged from 6 to 10 ug/m^3, a natural background of 1 ug/m^3 or less will not explain the observed relationships. Manmade local emissions would be expected to reflect ratios of sulfur dioxide to sulfate in flue gases or in plumes near their source. In plumes from coal-fired sources, such ratios are usually 50:1 to 100:1 with a few values as low as 20:1.[28]

in plumes from oil fired sources ratios as low as 10:1 might occur downwind, but the experimental data available is limited.[28-31] However, none of these ratios will account (even assuming frequent fumigation of the sites) for ratios of sulfur dioxide to sulfate near 1:1. There also is no experimental evidence that would suggest a much more rapid conversion of sulfur dioxide to sulfate in a plume from a nearby emission source in a nonurban environment than in an urban environment. This discussion is not meant to preclude local contributions to the concentrations at nonurban sites, but such contributions do not appear capable of accounting for the observed sulfur dioxide and sulfate concentration relationships.

Vanadium ratios between urban and nonurban sites should serve as a tracer for direct transport without further reaction of sulfur oxides from urban combustion sources in this part of the United States. The average sulfate concentrations near the surface in this part of the United States were 16 to 18 ug/m^3 during the 1960's. These are the only types of measurements available to use to represent the concentrations in the urban plume initially before travelling downwind. Using these concentrations and the vanadium ratios of 7:1 up to 13:1 lead to amounts of transported sulfate to the nonurban sites from within the urban areas of 1.2 to 2.6 ug/m^3. If there were any vanadium contributed enroute or in the vicinity of the nonurban sites, these vanadium ratios should be adjusted upward and the sulfate contribution downward.

The above computation also assumes that vanadium serves equally well as a tracer for coal-fired as for oil-fired combustion sources within the urban areas. Most of the nonutility sulfur oxide sources would be burning residual oil, with use of small amounts of distillate oil, and there would be a very small contribution from vehicular sources.[5] The oil-fired to coal-fired fuel usage ratio in utility sources was complex and changing. For the 1969-1973 period, during which detailed utility emission inventory information was available, the oil to coal sulfur oxide ratio over the entire region was 1:1.[6] However, almost three times as much sulfur oxide was associated with

coal as oil in the Philadelphia-Baltimore-Washington areas. It has been assumed that these varying gradients in oil to coal utility combustion-derived sulfur oxides will not greatly influence the averaged computations over the entire eastern region under consideration.

An averaged local contribution can be estimated with the use of several assumptions. It is assumed that the measured sulfur dioxide concentrations at the nonurban sites are largely of local origin. Involved in this assumption is the additional assumption that most of sulfur dioxide from distant large urban or utility plumes would be removed by conversion to sulfate or by dry deposition or precipitation before reaching these sites. It also must be assumed that the local contributions of sulfate can be estimated from use of urban sulfur dioxide to sulfate ratios. These urban sulfur dioxide to sulfate ratios by the late 1960's and early 1970's averaged near 4:1 at eastern sites. However, this ratio is not corrected for the portion of the sulfate measured at the surface which is not of local urban orgin. Such an estimate can be made from the earlier discussions of isolated and nonisolated air quality control regions as in the 6-8-ug/m^3 range. If these amounts of sulfate are subtracted, the resulting ratios would be 6:1 to 8:1. Using the sulfur dioxide concentrations at the nonurban sites with such ratios would lead to the estimate that about 1 ug/m^3 of sulfate was of local origin. Since part of the local sulfur dioxide could have originated from naturally produced hydrogen sulfide, this estimate of about 1 ug/m^3 would include any natural contribution. Some small amounts of sulfur dioxide from distant sources actually are likely to be transported to these nonurban sites, particularly the sulfur dioxide originating from elevated sources. Therefore, it is unlikely that the average local contribution of sulfate could be much higher than estimated here.

The midrange value for advected sulfate from distant sources of 1.5 ug/m^3 added to 1 ug/m^3 for local sulfate, accounts for about one-third of the measured sulfate averaged over these nonurban sites. The remaining available source must be sulfate formed by chemical conversion of sulfur dioxide during dispersion and transport of the sulfur dioxide from the

array of urban sources upwind of these nonurban sites. Based on the above estimates, about two-thirds of the sulfate measured at these nonurban sites can be attributed to sulfate formed by chemical reactions converting sulfur dioxide to sulfate during transport of pollutants from urban areas to nonurban locations. The contribution of urban sulfur dioxide area emissions would be expected to be less than elevated utility sources ton per ton because of the larger removal of sulfur dioxide by dry deposition from near-surface area sources of sulfur dioxide.

SECTION 6

GENERAL DISCUSSION

The urban and nonurban sulfate concentrations unlike sulfur dioxide and vanadium concentrations are relatively uniform throughout large portions of the eastern and midwestern United States east of the Mississippi River. Sulfur dioxide and vanadium concentrations show gradients of 3:1 to 6:1 between urban to suburban sites (Table 8) and gradients of from 5:1 to 14:1 between the urban and nonurban sites in the eastern United States (Tables 1 and 7). In contrast, sulfate concentrations show gradients of less than 2:1 between urban and suburban sites (Table 8) and of slightly more or less than 2:1 between urban and nonurban sites in the eastern United States (Tables 1 and 7).

The significantly less than proportional relationship between urban ambient sulfate concentrations in particular air quality control regions and sulfur oxide emissions in the same regions is demonstrated by two sets of results. The large reductions in urban sulfur dioxide emissions in air quality control regions between lower New England and Baltimore, Md. caused two to four-fold decreases in ambient sulfur dioxide concentrations while urban sulfate concentrations decreased by 20 to 40 percent. Comparisons of various air quality control regions having five- to ten-fold variations in sulfur oxide emissions showed only about a 30 percent variation in ambient sulfate concentrations.

How can this lack of proportionality be explained? A number of reasonable possibilities exist which may singly or in combination provide an adequate explanation. These factors are as follows: (2) the sulfate measured is not of local origin but is formed during transport from adjacent air quality control regions or more distant air quality control regions within the same geographical region of the United States, (3) the sulfate is not of local origin but is formed during transport from distant source in

another geographical region of the United States, (4) the sulfate is directly emitted within the same air quality region but the emission rate for sulfate is not directly proportional to the sulfur content of the fuel used (1) the mechanisms of formation in the atmosphere are such that on an annual average basis they do not result in sulfate formation being proportional to sulfur dioxide concentration.

The experimental results discussed in this report relate to factors (2) and (3), but the results cannot quantitatively define the distances over which transport occur. Therefore, the relative contributions from nearest neighbor air quality control regions, next nearest neighbor air quality control regions and more distant sources cannot be differentiated. However, experimental studies on the St. Louis, Mo. urban plume on individual experiment days demonstrate formation and transport of sulfate distances out to several hundred kilometers.[32,33] Measurements of the sulfur budget in a large power plant plume demonstrated 13% of the sulfur in particulate form at 40 km with the total sulfur mass in the plume conserved out to 50 to 100 km.[34] Analysis of 1974-75 sulfate episodes in the midwestern United States have been interpreted to be consistent with a contribution of isolated sources on a scale of 200 to 300 km.[35] Removal rates of sulfur oxides from urban and industrial plumes of 20 percent per hour have been reported leading to 1/e distances of less than 100 km over agricultural terrain in the midwestern United States.[34] Transport of sulfur containing particles over distances of 1000 to 2000 km over water have been reported in Northern Europe.[36,37]

These results strongly support the conclusions of this report and earlier analysis of monitoring data[1,2] that sources outside of a given air quality control region contribute significantly to the total sulfate loading within that region. The results suggest over land effective transport ranges of at least several hundred kilometers. Experimental results are lacking as to whether or not longer range transport can occur over land masses. If such longer range transport does not occur it must follow that rates of removal of sulfate particles over land[38-46] are substantially greater

than over water.[36,37]

The 4th factor suggests a lack of proportionality between sulfur in fuel and sulfate emissions. Recent measurements on various oil-fired boiler-fuel combinations indicate such a lack of proportionality with percentage of total sulfur as sulfate increasing as fuel sulfur content decreases.[31]

The increases in sulfate concentration or lack of trends at nonurban sites on or near the east coast of the United States are difficult to explain. There are consistent results demonstrating large decreases in ground level sulfur dioxide concentrations within urban areas. Total utility sulfur oxides emissions were decreasing substantially in almost all of the air quality control regions on or near the east coast from the late 1960's into the 1970's (1968-1973).[6] The air quality control regions in which several of these sites are located (Arcadia Natl. Park, Maine; Coos County, N. H.; Orange County, Vt.) have very small sulfur oxide emissions and the immediate surrounding areas very low population densities for the eastern United States. At the Orange County, Vt. site there was an increase in vanadium concentration between 1965-67 and 1970-72 which suggests increased importance of sources burning high vanadium fuel oil. However, the trend also suggests the possibility of contributions by long range transport from United States sulfur oxide sources which had increasing emissions in the midwestern United States or perhaps from sources outside of the United States.

The trends at the midwestern non-urban United States sites are reasonably consistent with the increases, particularly in utility sulfur oxide emissions in the air quality control regions in which the sites are located or from adjacent air quality control regions. The increases in sulfur oxide emissions in a significant number of midwestern air quality control regions east of the Mississippi River was quite substantial.[6]

The rates of conversion of sulfur oxides appear highly variable. However, slower rates of 1 to 2 percent per hour are sufficient to produce substantial sulfate concentrations during extraregional multiday transport periods. The stability of sulfates compared to sulfur dioxide with respect to further chemical reaction and dry deposition ensures appreciable transport without appreciable removal, particularly from elevated sources of emissions.

These conclusions have significance with respect to the capability to achieve reductions in ambient air sulfate concentrations. Substantial reductions of sulfur dioxide emissions within the presently constituted air quality control regions (AQCR) have resulted in only modest reductions in the concentrations of sulfates in the same AQCR. The analysis of available results indicates that substantial reductions of sulfur oxides emissions throughout large regions will be essential to achieving substantial reductions in the concentrations of ambient air sulfates in the eastern United States. Long-range transport and chemical transformation of sulfur oxide to sulfates appears responsible for such a requirement. The size of these regions needs to be defined, but probably these regions would be at least as large as the geographical regions used in this paper.

The lack of substantial variations of sulfate concentrations with large changes in patterns of sulfur oxide emissions has been discussed. Since many of these changes occur in western areas that differ with respect to meteorological and terrain aspects, the lack of large variations among such areas might be attributed to fortuitous balances among various parameters. However, the consistently low sulfate concentrations at almost all western sites strongly indicates that such low concentrations are most likely to be associated with low levels of sulfur oxide emissions through large adjacent regions or other factors leading to isolation.

The installation of new large clusters of utility capacity in western areas, if such installations emit substantial amounts of sulfur oxides, may lead to increases in sulfate concentrations at locations that are long distances downwind of such clusters. Detailed monitoring of the trend in

sulfates at a substantial number of selected western sites appears essential.

The present discussion is not meant to imply that precise quantitative experimental results are presently available to define several critical aspects of the sulfate problem. The rates of conversion of sulfur dioxide to sulfates within utility plumes, plumes from large nonutility point sources, and urban plumes need continuing experimental measurement. The relative contributions of utility sources, nonutility point sources, and area sources to surface-level concentrations of sulfate require much improved quantitation. Large-scale transport of sulfates in various geographical regions in the United States as a function of precipitation and other removal parameters has not been investigated, but urgently needs consideration. The impact of sulfates on visibility reduction, materials deterioration, water quality, and soil chemistry should be evaluated. Finally, the measurement instrumentation and other experimental techniques essential to the success of such field investigations must be improved.

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Table 2 (continued)

Site	Pollutant	1963-64	1964-65	1965-66	1966-67	1967-68	1968-69	1969-70	1970-71	1971-72	1972-73
Steubenville, Ohio	SO_2	[60][a]	62	60	56	51	42	[47][a]	48	[47][a]	48
	SO_4^{-2}	14.2	14.1	13.9	13.4	13.1	14.3	14.0	16.0	15.5	15.0
Cleveland, Ohio	SO_2	[58][a]	65	76	75	71	72	[65][a]	68	65	68
	SO_4^{-2}	15.9	14.3	13.1	13.5	14.8	17.0	[17.8][a]	[17.3][a]	16	16
Detroit, Mich.	SO_2	[36][a]	36	32	47	54	53	55	[45][a]	[37][a]	48
	SO_4^{-2}	14.2	15.3	12.9	12.9	12.7	14.0	13.5	15.4	13.9	[15.2][a]
Indianapolis, Ind.	SO_2	[56][a]	55	51	49	44	36	38	[42][a]	[35][a]	40
	SO_4^{-2}	13.4	14.0	13.2	13.0	12.1	12.4	11.9	12.5	12.1	[12.6][a]
Gary (Chicago), Ind.	SO_2	[58][a]	112	117	[88][a]	97	77	[77][a]	68	68	68
	SO_4^{-2}	18.4	17.7	16.7	16.5	16.3	15.6	16.7	17.9	18.2	18.2

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TABLE 5. [illegible] FOR SULFUR DIOXIDE AND SULFATES (NO INDICATES NOT DETERMINED) AT WESTERN SITES

Site	Pollutant	1963-65	1964-66	1965-67	1966-68	1967-69	1968-70	1969-71	1970-72	1971-73	1972-74
Denver, Colo.	SO_2	[1.9][a]	19	20	20	20	16	[16][a]	NO	NO	NO
	SO_4^{-2}	4.7	4.3	4.0	3.9	[3.9][a]	[4.5][a]	[4.8][a]	5.4	6.7	[7.5][a]
Salt Lake City, Utah	SO_2	[15][a]	16	16	18	21	18	[18][a]	NO	NO	NO
	SO_4^{-2}	7.9	7.6	6.2	5.2	5.3	5.8	6.7	6.5	7.5	[7.3][a]
Casper, Wyo.	SO_2	NO	NO	NO	[17][a]	16	11	[12][a]	NO	NO	NO
	SO_4^{-2}	NO	NO	NO	[3.2][a]	4.0	4.6	5.3	5.1	5.5	[6.3][a]
Yuma, Ariz.	SO_2	NO	NO	NO	[5][a]	8	[8][a]	NO	NO	NO	NO
	SO_4^{-2}	[5.0][a]	[5.4][a]	5.1	4.5	6.6	7.6	7.9	6.9	6.5	7.0
Oklahoma City Okla.	SO_2	NO	NO	[10][a]	10	10	[9][a]	NO	NO	NO	NO
	SO_4^{-2}	NO	[5.3][a]	5.1	4.2	4.1	4.8	[5.7][a]	[6.6][a]	NO	[5.6][a]
Houston, Texas	SO_2	NO	NO	NO	NO	NO	[11][a]	NO	NO	NO	NO
	SO_4^{-2}	[6.6][a]	6.5	7.4	7.0	8.0	7.2	7.7	7.0	8.3	9.0

[continued]

Table 5 (continued)

Site	Pollutant	1983-85	1984-86	1985-87	1986-88	1987-89	1988-90	1989-91	1990-92	1991-93	1992-94
[illegible], Texas	SO_2	[illegible]	[illegible]	[illegible]	[16][a]	15	[13][a]	[illegible]	[illegible][a]	[illegible][a]	[illegible]
	SO_4^{-2}	[illegible]	[illegible]	[illegible]	[7.1][a]	8.0	9.1	10.7	11.8	11.7	[11.4][a]
[illegible], Ariz.	SO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible][a]	[illegible]	[illegible]	[illegible]	[illegible]
	SO_4^{-2}	[5.8][a]	4.9	4.7	4.9	4.2	[4.7][a]	[5.1][a]	[5.2][a]	6.0	6.2
Regional averages	SO_2	-	-	-	15	15	12	-	[illegible]	[illegible]	[illegible]
	SO_4^{-2}	-	-	-	4.9	5.5	6.0	6.7	6.9	[7.5]	7.4

[a]Assessments available for only 2 of 3 years.

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TABLE 2. [illegible]

Site	Series	Soil layer	1985-87	1986-88	1987-89	1988-90	1989-91	1990-92	1991-93	1992-94
[illegible]	[illegible]	SO_4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7	[illegible]	[illegible]
		SO_4^{-2}	6.1	5.8	5.7	5.9	5.9	6.5	6.4	6.5
		Y	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		SO_4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		SO_4^{-2}	6.0	6.4	5.6	5.7	5.6	7.9	8.3	8.5
		Y	[illegible]	[illegible]	[illegible]	.31	.31	[illegible]	[illegible]	[illegible]
[illegible]		SO_4^{-2}	6.6	7.2	7.2	7.1	7.9	8.7	9.4	9.6
		Y	[illegible]	[illegible]	[illegible]	.36	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		SO_4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		SO_4^{-2}	10.7	9.6	9.6	9.1	8.9	9.0	9.3	[illegible]
		Y	[illegible]	[illegible]	[illegible]	.34	.32	[illegible]	[illegible]	[illegible]

(continued)

Table 7 (continued)

Site	Region	Pollutant	1965-67	1966-68	1967-69	1968-70	1969-71	1970-72	1971-73	1972-74
Kent Co., Del.	Urban Rural	SO_2	NC	NC	(15)[b]	(16)[b]	(17)[b]	NC	NC	NC
		SO_4^{-2}	10.2	10.2	(10.2)[b]	NC	NC	NC	NC	NC
		r	(0.258)[b]	0.255	(0.307)[b]	NC	NC	NC	NC	NC
Calvert Co., Md.		SO_2	NC	NC	10	10	(10)[b]	NC	NC	NC
		SO_4^{-2}	9.5	10.3	(10.3)[b]	(10.3)[b]	NC	NC	(11.9)[b]	11.7
		r	0.205	0.259	0.302	.33	NC	NC	NC	NC
Regional averages		SO_2	NC	NC	10	(12)[c]	(12)[c]	NC	NC	NC
		SO_4^{-2}	8.1	8.2	8.4	(7.8)[c]	(7.7)[c]	(8.1)[c]	(8.4)[c]	(8.4)[c]
		r	0.265	0.27	0.33	(0.33)[c]	(.335)[c]	NC	NC	NC

(continued)

Table 7 (continued)

Site	Region	Pollutant	1965-67	1966-68	1967-69	1968-70	1969-71	1970-72	1971-73	1972-74
Jefferson Co., N. Y.	Midwest (east of Mississippi)	SO_4^{-2}	[6.8][a]	7.9	8.8	9.5	8.7	[9.5][a]	[a]	[a]
Clarion Co., Pa.		SO_4^{-2}	8.7	9.0	9.5	10.4	10.1	11.1	11.1	[12.4][a]
Warren Co., Ind.		SO_4	[a]	[a]	[12][a]	11	[12][a]	[10][a]	[a]	[a]
		SO_4^{-2}	[6.5][a]	7.6	7.9	8.4	8.3	8.4	8.5	[8.1][a]
Parke Co., Ind.		SO_4^{-2}	7.1	6.8	7.2	9.7	11.4	12.3	12.7	[13.5][a]
National averages		SO_4^{-2}	7.3	7.8	8.1	[9.5][a]	[9.9][a]	[10.8][a]	[11.2][a]	[11.5][a]
Shenandoah Mt., Va. [Shenandoah, Page Co.]	Southeast	SO_4	[a]	[a]	[10][a]	9	[8][a]	[7][a]	[8][a]	[a]
		SO_4^{-2}	6.8	6.7	9.2	10.2	10.6	9.2	9.9	10.9
Coon Hollow, N. C.		SO_4^{-2}	7.0	6.7	7.5	9.8	10.4	11.6	[a]	[a]
Richland Co., S. C.		SO_4^{-2}	[6.7][a]	8.1	8.9	[9.4][a]	[9.8][a]	[8.7][a]	7.8	7.5

(continued)

Table 7 (continued)

Site	Species	Pollutant	1965-67	1965-68	1967-69	1969-70	1969-71	1970-72	1971-73	1970-73
Jackson Co., Miss.	Deciduous	SO_4^{-2}	5.4	5.8	[5.5][a]	ND	ND	[7.1][a]	7.7	8.9
Montgomery Co., Ark.		SO_4^{-2}	[3.7][a]	3.6	4.9	5.5	5.7	5.9	6.6	7.4
Regional average		SO_4^{-2}	5.4	6.7	7.2	[9.3][c]	[8.4][c]	[8.4][c]	[7.4][c]	[8.7][c]
Shannon Co., Mo.	Pollen, [sect. of Pinaceae]	SO_4	ND	ND	ND	ND	ND	[7][b]	ND	ND
		SO_4^{-2}	5.0	4.8	5.4	5.7	5.9	6.5	6.3	6.6
Texas Co., Mo.		SO_4^{-2}	2.6	1.8	2.7	2.9	3.1	2.3	2.2	2.6
Black Hills Nat. Park, S. D.		SO_4^{-2}	1.9	1.5	1.4	[1.4][a]	[1.3][a]	[2.4][a]	2.4	[2.3][a]
Regional average		SO_4^{-2}	3.1	2.7	3.2	3.3	3.8	3.8	3.6	3.8
White Pine Co., Nev.	Pinaceae	SO_4^{-2}	2.8	1.7	1.3	1.9	2.4	[2.4][a]	[1.9][a]	2.1
Yellowstone Nat. Pk., Wyo.		SO_4^{-2}	1.5	1.4	1.7	[2.0][a]	[2.1][a]	ND	ND	ND

(continued)

Table 7 (continued)

Site	Region	Pollutant	1965-67	1966-68	1967-69	1968-70	1969-71	1970-72	1971-73	1972-74
Glacier Natl. Pk., Mont.	Northern	SO_4^{-2}	2.0	1.6	1.5	[1.6][a]	[1.7][a]	[2.1][a]	2.0	[2.1][a]
Boise Co., Idaho		SO_4^{-2}	[1.5][a]	[1.5][a]	1.3	1.7	2.2	2.3	[2.4][a]	[illegible]
Regional average		SO_4^{-2}	1.7	1.2	1.5	[1.7][a]	[2.1][a]	[2.2][a]	[2.1][a]	-
Champion Co., Ala.	Southeast	SO_4^{-2}	4.5	4.2	4.5	6.3	7.0	7.7	5.6	5.7
Nacogdoches Co., Texas		SO_4^{-2}	2.9	3.9	6.0	6.7	7.4	6.2	5.7	5.5
Grand Canyon Pk., Ariz.		SO_4^{-2}	2.0	1.8	2.0	2.6	3.1	[2.8][a]	[2.7][a]	[2.4][a]
Regional average		SO_4^{-2}	3.5	3.3	4.2	5.2	5.8	5.6	4.7	4.5
Redwood Co., Calif.	West coast	SO_4^{-2}	2.0	2.6	3.4	3.7	3.9	[illegible]	[illegible]	[illegible]
Curry Co., Ore.		SO_4^{-2}	3.3	3.3	3.1	3.8	3.8	4.1	4.1	[4.2][a]
Regional average		SO_4^{-2}	3.0	3.0	3.2	3.8	3.9	-	-	-

[a] Measurements available for only 2 of 3 years.

[b] Measurements available for only 1 year.

[c] Measurements based on 4 sites.

[d] Measurements based on 3 sites.

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